

## PATENT ABSTRACTS OF JAPAN

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## (54) PRODUCTION OF (METH)ACRYLAMIDE POLYMER

## (57)Abstract:

PURPOSE: To produce a (meth)acrylamide polymer usable as a thickener, a flocculant, a strength additive, a yield improver and a freeness improver used in the paper industry, a dispersion stabilizer for various suspensions, a soil conditioner or a sustained-release material even when the concentration of the polymerizable monomer is high.

CONSTITUTION: The process for producing a (meth)acrylamide polymer comprises allowing a cross-linked polyelectrolyte to absorb an aqueous solution containing (meth)acrylamide alone or both this monomer and at least one monomer copolymerizable therewith and polymerizing the polymerizable monomers within the swollen cross-linked polyelectrolyte.

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CLAIMS

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[Claim(s)]

[Claim 1] The manufacture approach of the acrylamide system polymer characterized for acrylamide by independent or (meta) carrying out the polymerization of the polymerization nature monomer into the crosslinked polymer electrolyte which was made to absorb the water solution which comes to contain acrylamide, acrylamide (meta), a kind to copolymerize, or two sorts or more of polymerization nature monomers, and swelled it as a polymerization nature monomer (meta) at a crosslinked polymer electrolyte (meta).

[Claim 2] The manufacture approach according to claim 1 that a crosslinked polymer electrolyte is the alkali-metal salt of an acrylic-acid system polymer bridge formation object.

[Claim 3] The manufacture approach according to claim 1 that the weight ratios of a crosslinked polymer electrolyte and a polymerization nature monomer are the former / latter = 10 / 90 - 90 / 10, and the water-solution concentration of a polymerization nature monomer is 5 - 50 % of the weight.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the new manufacture approach of an acrylamide (meta) system polymer. It is related with the new manufacture approach of the acrylamide system polymer currently widely used for a thickener, a flocculant, the paper reinforcing agent in pulp and paper industry, the yield improver, the filtration improvement agent, the distributed stabilizer of various suspension solutions, the soil conditioner, etc. in detail (meta).

[0002]

[Description of the Prior Art] Conventionally, the acrylamide (meta) system polymer is mainly manufactured by aqueous polymerization, and is obtained in the state of a uniform water solution. Moreover, in aqueous polymerization, since a product serves as gel which carried out water and handling becomes it is remarkable and difficult as monomer concentration becomes high, what has high monomer concentration cannot be manufactured industrially.

[0003] Therefore, although an acrylamide (meta) system polymer is diluted, and it is provided as a low concentration solution or disintegration is dried and carried out, in dealing with it by low concentration, an transportation cost becomes high, and heat energy huge for desiccation disintegration is needed uneconomically, and also it has problems, like insolubilization by thermal three-dimensions bridge formation takes place.

[0004] Moreover, although the manufacture approach of the dispersion liquid of the acrylamide system polymer by the emulsion polymerization of a water-in-oil type or the suspension polymerization in the inside of a hydrophobic solvent is also learned, since the hydrophobic organic solvent currently used by these approaches has a strong odor while it is dangerous, it has problems, like a large amount of costs are needed for each manufacturing facility of a polymerization and separation from the problem of work environment. It is known from before that water soluble polymers, such as an acrylamide (meta) system polymer, will cause other water soluble polymers and interactions under water, and will produce phase separation on the other hand. For example, for example, if a polyalkylene glycol solution and a polyacrylamide water solution are mixed, phase separation will arise. However, only by applying the interaction reported, the dispersion liquid of the acrylamide system polymer which is rich in dispersibility and a fluidity (meta) are not obtained, and since we were anxious about the effect of the water soluble polymer together put on product performance, they have not resulted in utilization.

[0005]

[Means for Solving the Problem] this invention persons repeated examination wholeheartedly about the manufacture approach of an acrylamide (meta) system polymer from such a background. consequently, when a crosslinked polymer electrolyte is made to absorb the water solution containing the polymerization nature monomer which uses acrylamide (meta) as a principal component and it carries out a polymerization In order that the acrylamide (meta) system polymer generated with advance of a polymerization may carry out phase separation by the interaction with a crosslinked polymer electrolyte into a crosslinked polymer electrolyte, may deposit in the shape of a particle one by one and may form uneven structure, Even when a polymerization nature monomer was high concentration, the thing from which the water solution

containing the polymerization nature monomer absorbed in the crosslinked polymer electrolyte hyperviscosity--izes to gel, and prevents advance of a polymerization and for which an acrylamide system polymer can be manufactured that there is nothing (meta) was found out. This invention is completed based on the starting new knowledge.

[0006] That is, this invention relates acrylamide to a crosslinked polymer electrolyte as a polymerization nature monomer (meta) at independent or (meta) the manufacture approach of an acrylamide system polymer characterized by carrying out the polymerization of the polymerization nature monomer into the crosslinked polymer electrolyte which was made to absorb the water solution which comes to contain acrylamide, acrylamide (meta), a kind to copolymerize, or two sorts or more of polymerization nature monomers, and was swollen (meta).

[0007] In this invention, acrylamide is used as an indispensable component as a polymerization nature monomer (meta). (Meta) acrylamide -- the thing of acrylamide and/or methacrylamide -- saying -- this invention -- setting (meta) -- it is the same semantics as the following. Generally, acrylamide is used. \*\* (meta) acrylamide can be used independently, and also it can also be used together with acrylamide (meta), a kind to copolymerize, or two sorts or more of polymerization nature monomers. (Meta) As acrylamide and a polymerization nature monomer to copolymerize, at least one sort chosen from an anionic partial saturation monomer, a cationic partial saturation monomer, a nonionic partial saturation monomer, and a cross-linking partial saturation monomer is raised.

[0008] As an anionic partial saturation monomer, alkali-metal salts, such as sodium salt of organic sulfonic-acids [, such as dicarboxylic acid; vinyl sulfonic acids such as monocarboxylic acid; maleic acids, such as an acrylic acid, a crotonic acid, and an allyl compound (meta) carboxylic acid, boletic acid, an itaconic acid, and muconic acid, a styrene sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, and an allyl compound (meta) sulfonic acid, ]; or these various organic acids and potassium salt, etc. are raised, for example (meta), it is independent in these one sort, or two or more sorts can be used.

[0009] As a cationic partial saturation monomer, to a typical thing, dimethylaminoethyl (meta) acrylate, Diethylaminoethyl (meta) acrylate, dimethylaminopropyl (meta) acrylamide, The partial saturation monomers which have the third class amino groups, such as diethylamino propyl (meta) acrylamide and allylamine (meta), or those hydrochloric acids, The salts of inorganic acids, such as a sulfuric acid and an acetic acid, or an organic acid, or this the third class amino-group content partial saturation monomer and methyl chloride, The partial saturation monomer containing the quarternary ammonium salt obtained by the reaction with the fourth class-ized agents, such as benzyl chloride, a dimethyl sulfate, and epichlorohydrin, etc. is raised, it is independent in these kinds, or two or more sorts can be used.

[0010] As a nonionic partial saturation monomer, the alkyl ester (carbon numbers 1-8 of an alkyl group) of said anionic partial saturation monomer, acrylonitrile, styrene, vinyl acetate, the methyl vinyl ether, allyl alcohol (meta), etc. are raised. These are independent in a kind or can use two or more sorts.

[0011] Moreover, the following are raised as a typical thing of a cross-linking partial saturation monomer. As a 2 functionality partial saturation monomer, for example, ethylene GURIKORUJI (meta) acrylate, Di(meth)acrylate, such as diethylene GURIKORUJI (meta) acrylate and TORIECHIRENGURIKORUJI (meta) acrylate Methylenebis (meta) acrylamide, ethylene screw (meta) acrylamide, Screw (meta) acrylamides, such as hexa methylenebis (meta) acrylamide Divinyl ester, such as an adipic-acid divinyl and a sebacic-acid divinyl Allyl compound (meta) (meta) acrylate and epoxy (meta) acrylate Urethane (meta) acrylate, N-methylol (meta) acrylamide, JI (meta) allylamine, JI (meta) allyl compound dimethylannmonium, JI (meta) allyl compound phthalate, a JI (meta) allyl compound KUOREN date, a divinylbenzene, etc. are raised. As a 3 functionality monomer, moreover, 1, 3, 5-Tori (meta) acryloyl hexahydro-S-triazine, Tori (meta) allyl compound isocyanurate, the Tori (meta) allylamine, Tori (meta) allyl compound trimellitate, N, and N-JI (meta) allyl compound (meta) acrylamide etc. as a 4 functionality partial saturation monomer Tetramethylolmethane tetrapod (meta) acrylate, tetrapod (meta) allyl compound pyromellitate, N and N, N', N'-tetrapod (meta) allyl compound-1,4-diaminobutane, a tetrapod (meta) allylamine salt, tetrapod (meta) allyloxy ethane, etc. are

raised. These are independent in a kind or can use two or more sorts.

[0012] the total mol sum of the polymerization nature monomer in which the amount of the aforementioned (meta) acrylamide and the polymerization nature monomer used to copolymerize contains acrylamide (meta) -- usually -- less than [ 50 mol % ] -- it is less than [ 20 mol % ] preferably. (Meta) Since the rate of acrylamide decreases when the amount of acrylamide and the polymerization nature monomer used to copolymerize exceeds 50-mol % (meta), the phase separation by the interaction with a crosslinked polymer electrolyte stops arising, and the particle of an acrylamide (meta) system polymer is no longer obtained. in addition, the application of the acrylamide system polymer with which an anionic partial saturation monomer, a cationic partial saturation monomer, a nonionic partial saturation monomer, and a cross-linking partial saturation monomer can be used together with acrylamide (meta) combining a kind or two sorts or more, respectively, and the operating rate is obtained (meta) etc. -- taking into consideration -- the total mol sum of a polymerization nature monomer -- usually -- 50-mol% of within the limits -- proper -- determining -- \*\*\*\*ing . However, when using a cross-linking partial saturation monomer, it is good less than [ of the total mol sum of a polymerization nature monomer / usual 10 mol % ], and to consider as 0.01-5-mol % preferably. In exceeding ten-mol %, in order that the whole water solution containing the polymerization nature monomer absorbed in the crosslinked polymer electrolyte may construct a bridge, the particle of an acrylamide (meta) system polymer is not obtained.

[0013] In this invention, the salt of the various polymer bridge formation objects obtained by carrying out the polymerization of a kind of the anionic partial saturation monomer of said instantiation which has a carboxylic acid and/or a sulfonic acid, for example or two sorts or more, and the cross-linking partial saturation monomer as a crosslinked polymer electrolyte which makes the polymerization nature monomer which uses acrylamide (meta) as a principal component absorb is raised. As an anionic partial saturation monomer, an acrylic acid is desirable. Moreover, as a cross-linking partial saturation monomer, ethylene GURIKORUJI (meta) acrylate etc. is desirable also in said instantiation. The amount of the amount of cross-linking partial saturation single used is suitably determined in consideration of the water-absorption-power force of a crosslinked polymer electrolyte, and is usually about [ of the total mol sum of the partial saturation monomer which constitutes a crosslinked polymer electrolyte ] 0.05-5 mol %.

[0014] If the water-absorption-power force of this crosslinked polymer electrolyte is extent which can take the condition of happening only in the crosslinked polymer electrolyte with which the polymerization of the polymerization nature monomer which could absorb to homogeneity at the whole crosslinked polymer electrolyte, and was absorbed swelled the water solution containing a polymerization nature monomer, especially a limit will not be carried out but will usually be preferably made into five to 20 times about 1 to 100 times. In order that a crosslinked polymer electrolyte cannot absorb the water solution with which the water-absorption-power force contains a polymerization nature monomer in less than 1 time and the polymerization of a polymerization nature monomer may break out by underwater [ besides a crosslinked polymer electrolyte ], a hyperviscous gel object is obtained and it is not desirable. Moreover, when the water-absorption-power force exceeds 100 times and the water solution which contains a polymerization nature monomer in a crosslinked polymer electrolyte is added, while the location where the water solution concerned will be absorbed by only the contact front face with a crosslinked polymer electrolyte, and a polymerization advances in a crosslinked polymer electrolyte becomes an ununiformity, since the presentation ratio of the crosslinked polymer electrolyte and polymerization nature monomer which were set up, and water is changed, it is not desirable. In addition, the water-absorption-power force is the value which put the crosslinked polymer electrolyte into the ion exchange water of an overlarge, filtered after 30 minutes, and was calculated by the degree type. Water-absorption-power force (twice) =(weight of ion exchange water with which crosslinked polymer electrolyte absorbed water)/(weight of a polyelectrolyte).

[0015] Moreover, what copolymerized at least one sort which will use together with an anionic partial saturation monomer if it is within the limits in which the acrylamide system polymer

obtained (meta) deposits by the shape of a particle by the interaction with the crosslinked polymer electrolyte concerned, and is chosen from amide group content partial saturation monomers, such as a cationic partial saturation monomer of said instantiation, a nonionic partial saturation monomer, and acrylamide (meta), is sufficient as the crosslinked polymer electrolyte of this invention. usually, the total mol sum of the partial saturation monomer from which the rate of the copolymerization monomer used together with an anionic partial saturation monomer constitutes a crosslinked polymer electrolyte -- receiving -- usually -- less than [ 30 mol % ] -- it is less than [ 10 mol % ] preferably. Moreover, what reformed the front face of a crosslinked polymer electrolyte by the cross linking agent which has a carboxylic acid etc. and two or more functional groups which react is sufficient as the crosslinked polymer electrolyte of this invention.

[0016] Although especially the class of salt of the polymer bridge formation object which constitutes a crosslinked polymer electrolyte is not limited, in this invention, alkali-metal salts, such as sodium salt or potassium salt, are desirable. moreover, the neutralization index of a carboxylic acid and/or a sulfonic acid -- usually -- 60-100-mol % -- it is 70-100-mol % preferably. It takes place [ formation of the particle of the acrylamide system polymer according / a neutralization index / to an interaction (meta) ] easily and is not usually desirable less than [ 60 mol % ]. In addition, formation of carboxylate and/or a sulfonate may be performed in the phase of an anionic partial saturation monomer, and you may carry out, after manufacturing a polymer bridge formation object. That is, as a crosslinked polymer electrolyte of this invention, it is desirable to use the alkali-metal salt of an acrylic-acid system polymer bridge formation object.

[0017] Next, the manufacture approach of the acrylamide (meta) system polymer of this invention is explained in detail. although the amount of the crosslinked polymer electrolyte used changes with a presentation and degree of cross linking of the crosslinked polymer electrolyte concerned, the presentation ratio of a polymerization nature monomer, polymerization concentration, and other polymerization conditions -- usually -- the weight ratio of a crosslinked polymer electrolyte and a polymerization nature monomer -- usually -- the former / latter = 10 / 90 - 90/10 -- it is 20 / 80 - 80/20 preferably. If the rate of a crosslinked polymer electrolyte separates from this range, an acrylamide (meta) system polymer cannot be obtained by the shape of a particle in a crosslinked polymer electrolyte.

[0018] Moreover, the water-solution concentration of a polymerization nature monomer is usually 15 - 40 % of the weight preferably five to 50% of the weight. It is not desirable in order for a rate of polymerization to become quick too much, and for it to become impossible to control polymerization temperature by generation of heat, and for it to become impossible for a crosslinked polymer electrolyte to fully absorb the water solution of a polymerization nature monomer and to concur with the polymerization in the crosslinked polymer electrolyte exterior, if water-solution concentration exceeds 50 % of the weight. A rate of polymerization becomes extremely slow, and the phase separation by the interaction of the acrylamide (meta) system polymer and crosslinked polymer electrolyte which were generated stops arising, and it becomes impossible moreover, for it to become impossible to obtain the amount (meta) acrylamide system polymer of macromolecules, and to obtain an acrylamide (meta) system polymer according to the shape of a particle at less than 5 % of the weight.

[0019] The method of carrying out the polymerization of said polymerization nature monomer, and manufacturing an acrylamide (meta) system polymer makes the water solution containing a polymerization nature monomer absorb to a crosslinked polymer electrolyte, and can adopt various well-known approaches and the same approach as it conventionally except for performing a polymerization in the swollen crosslinked polymer electrolyte. For example, a crosslinked polymer electrolyte, a polymerization nature monomer, and water are taught to a predetermined reaction container, the usual radical polymerization initiators, such as a redox system polymerization initiator of the form which combined persulfate, such as potassium persulfate and ammonium persulfate, or these and the reducing agent like a sodium hydrogensulfite, are added, and the approach of warming, the approach of adding and carrying out UV irradiation of the photopolymerization initiator, etc. are raised under churning.

[0020] The amount used, such as a radical polymerization initiator, is usually 0.01–10–mol % to a polymerization nature monomer. moreover, pH of the crosslinked polymer electrolyte water solution containing the polymerization nature monomer at the time of a polymerization -- usually -- 6–10 -- it is 7–8 preferably, and it is necessary to set up the neutralization index of the carboxylic acid of said crosslinked polymer electrolyte, and/or a sulfonic acid so that it may go into this range Since it produces hydrolysis of an acrylamide system polymer in phase separation's stopping being able to happen easily when pH is lower than 6, and exceeding 10 (meta), it is not desirable. Although the temperature of a polymerization changes with presentations and those concentration of the class of radical polymerization initiator, a polymerization nature monomer, and a crosslinked polymer electrolyte and it cannot generally \*\*\*\*\* it is usually within the limits of 25–90 degrees C, and a polymerization is performed to the bottom of such a condition for 1 to 12 hours. In addition, on the occasion of a polymerization, a water-soluble chain transfer agent, a surfactant, a salt, etc. can be used for arbitration as an additive if needed. Although the amount of these additives used changes with applications of the acrylamide system polymer obtained (meta) etc. and cannot be limited especially, generally it is 10 or less % of the weight to a polymerization nature monomer.

[0021] The weight average molecular weight of the acrylamide (meta) system polymer obtained in this way is usually 100,000 to about 20 million. Moreover, an acrylamide (meta) system polymer produces phase separation by the interaction with a crosslinked polymer electrolyte, and deposits by the shape of a particle in the swollen crosslinked polymer electrolyte. The particle of the obtained acrylamide (meta) system polymer is in the condition contained in the crosslinked polymer electrolyte, and direct drying can be carried out by warm air etc., or it can be made to be able to dry, after permuting by water soluble solvents, such as an acetone and a methanol, and it can also be fine-particles-ized. Moreover, the acrylamide (meta) system polymer contained by the shape of a particle in the crosslinked polymer electrolyte is gradually eluted by switching on a crosslinked polymer electrolyte underwater. (Meta) The temperature of water, pH, salt concentration, etc. can adjust the rate at which an acrylamide system polymer is eluted.

[0022]

[Example] Although an example explains this invention concretely below, this invention is not limited to this.

[0023] 200g (11.62 times as many water-absorption-power force as this) of example 1 sodium-polyacrylate bridge formation object powder was put into 3L reaction containers which attached a stirrer, nitrogen installation tubing, the thermometer, and the reflux condenser, after making the water solution which becomes this from acrylamide 100g, 700g of ion exchange water, and 0.8g of ammonium persulfates add and swell, except for dissolved oxygen, 3.5g of sodium-pyrosulfite water solutions was added 1% of the weight through nitrogen gas at the room temperature, and the polymerization was carried out at 45 degrees C under churning for 6 hours. The product was supplied in the acetone of 2L after polymerization termination, and the polyacrylamide particle in filtration and the condition of having carried out reduced pressure drying and having contained in the crosslinked polymer electrolyte was obtained. The weight of the dry matter (product) concerned was 289g, and the water-absorption-power force was 7.62 times. The electron microscope photograph of the dry matter concerned is as being shown in drawing 1, and it is admitted that the polyacrylamide particle exists in the condition of having contained in the crosslinked polymer electrolyte.

[0024] 200g (9.54 times as many water-absorption-power force as this) of example 2 sodium-polyacrylate bridge formation object powder It puts into 3L reaction containers which attached a stirrer, nitrogen installation tubing, the thermometer, and the reflux condenser. To this, acrylamide 100g, methylenebis acrylamide 1.08g, After making the water solution which consists of 8.68g of sodium methallylsulfonate, 700g of ion exchange water, and 0.8g of ammonium persulfates add and swell, Except for dissolved oxygen, 3.5g of sodium-pyrosulfite water solutions was added 1% of the weight through nitrogen gas at the room temperature, and the polymerization was carried out at 45 degrees C under churning for 6 hours. The product was supplied in the acetone of 2L after polymerization termination, and the polyacrylamide particle in filtration and the condition of having carried out reduced pressure drying and having contained in

the crosslinked polymer electrolyte was obtained. The weight of the dry matter (product) concerned was 301g, and the water-absorption-power force was 4.9 times. The electron microscope photograph of the dry matter concerned is as being shown in drawing 2, and it is admitted that the polyacrylamide particle exists in the condition of having contained in the crosslinked polymer electrolyte.

[0025]

[Effect of the Invention] In order that phase separation of the acrylamide (meta) system polymer generated by the manufacture approach of this invention may be carried out by the interaction with a crosslinked polymer electrolyte into a crosslinked polymer electrolyte, it may deposit in the shape of a particle one by one and may form uneven structure, the whole water solution containing the polymerization nature monomer absorbed in the crosslinked polymer electrolyte hyperviscosity-izes it to gel, and it does not check advance of a polymerization. Therefore, even when a polymerization nature monomer is high concentration, an acrylamide (meta) system polymer can be manufactured.

[0026] The acrylamide (meta) system polymer formed in the crosslinked polymer electrolyte which is the product of the manufacture approach of this invention can be widely used for the thickener with which elution could be carried out to underwater, for example, the acrylamide system polymer was used conventionally, a flocculant, the paper reinforcing agent in pulp and paper industry, a yield improver, a filtration improvement agent, the distributed stabilizer of various suspension solutions, a soil conditioner, etc. Moreover, the exit velocity from the crosslinked polymer electrolyte of a forming [in the shape of a particle]-in crosslinked polymer electrolyte (meta) acrylamide system polymer can be adjusted with temperature, pH, salt concentration, etc., and can also be used as a sustained-release ingredient of an acrylamide (meta) system polymer.

[0027] On the other hand, the product of the manufacture approach of this invention can also be considered to be the improvements of a crosslinked polymer electrolyte when there are many operating rates of a crosslinked polymer electrolyte, and it can be used as the absorptivity grant agent to fluid amelioration agents, such as a high absorptivity polymer and a drainage system coating, plastics, etc., an antistatic agent, a separation ingredient, etc. When using for these applications, it is effective by using a cross-linking partial saturation monomer as a polymerization nature monomer that an acrylamide (meta) system polymer also constructs a bridge. In addition, although the approach of absorbing a water soluble polymer and making it construct a bridge for amelioration of a crosslinked polymer electrolyte etc. was learned, the constraint of the molecular weight of a water soluble polymer or the amount of installation which can be introduced was received, and it had become a problem that it can introduce only into the front face of a crosslinked polymer electrolyte. Furthermore, although it did not necessarily have a crosslinked polymer electrolyte and each features of a water soluble polymer by the conventional approach since the water soluble polymer covered the front face of a crosslinked polymer electrolyte and it was made homogeneity into the crosslinked polymer electrolyte The acrylamide system polymer obtained by the manufacture approach of this invention (meta) Since the uneven structure which deposited in homogeneity in the shape of a particle within the crosslinked polymer electrolyte is introduced, the crosslinked polymer electrolyte and the bridge formation (meta) acrylamide system polymer hold each features as it is, and can use for various kinds of applications which harnessed each features.

[0028] Furthermore, since the manufacture approach of this invention makes the swollen crosslinked polymer electrolyte absorb a polymerization nature monomer and carries out a polymerization to it, it is possible also for a fine-particles-like polymerization and a sheet-like polymerization, and fine-particles-izing of a product is also easy.

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TECHNICAL FIELD

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[Industrial Application] This invention relates to the new manufacture approach of an acrylamide (meta) system polymer. It is related with the new manufacture approach of the acrylamide system polymer currently widely used for a thickener, a flocculant, the paper reinforcing agent in pulp and paper industry, the yield improver, the filtration improvement agent, the distributed stabilizer of various suspension solutions, the soil conditioner, etc. in detail (meta).

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## EFFECT OF THE INVENTION

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[Effect of the Invention] In order that phase separation of the acrylamide (meta) system polymer generated by the manufacture approach of this invention may be carried out by the interaction with a crosslinked polymer electrolyte into a crosslinked polymer electrolyte, it may deposit in the shape of a particle one by one and may form uneven structure, the whole water solution containing the polymerization nature monomer absorbed in the crosslinked polymer electrolyte hyperviscosity-izes it to gel, and it does not check advance of a polymerization. Therefore, even when a polymerization nature monomer is high concentration, an acrylamide (meta) system polymer can be manufactured.

[0026] The acrylamide (meta) system polymer formed in the crosslinked polymer electrolyte which is the product of the manufacture approach of this this invention can be widely used for the thickener with which elution could be carried out to underwater, for example, the acrylamide system polymer was used conventionally, a flocculant, the paper reinforcing agent in pulp and paper industry, a yield improver, a filtration improvement agent, the distributed stabilizer of various suspension solutions, a soil conditioner, etc. Moreover, the exit velocity from the crosslinked polymer electrolyte of a forming [ in the shape of a particle ]-in crosslinked polymer electrolyte (meta) acrylamide system polymer can be adjusted with temperature, pH, salt concentration, etc., and can also be used as a sustained-release ingredient of an acrylamide (meta) system polymer.

[0027] On the other hand, the product of the manufacture approach of this invention can also be considered to be the improvements of a crosslinked polymer electrolyte when there are many operating rates of a crosslinked polymer electrolyte, and it can be used as the absorptivity grant agent to fluid amelioration agents, such as a high absorptivity polymer and a drainage system coating, plastics, etc., an antistatic agent, a separation ingredient, etc. When using for these applications, it is effective by using a cross-linking partial saturation monomer as a polymerization nature monomer that an acrylamide (meta) system polymer also constructs a bridge. In addition, although the approach of absorbing a water soluble polymer and making it construct a bridge for amelioration of a crosslinked polymer electrolyte etc. was learned, the constraint of the molecular weight of a water soluble polymer or the amount of installation which can be introduced was received, and it had become a problem that it can introduce only into the front face of a crosslinked polymer electrolyte. Furthermore, although it did not necessarily have a crosslinked polymer electrolyte and each features of a water soluble polymer by the conventional approach since the water soluble polymer covered the front face of a crosslinked polymer electrolyte and it was made homogeneity into the crosslinked polymer electrolyte Since the uneven structure to which the acrylamide system polymer obtained by the manufacture approach of this invention (meta) deposited in homogeneity in the shape of a particle within the crosslinked polymer electrolyte is introduced, the crosslinked polymer electrolyte and the bridge formation (meta) acrylamide system polymer hold each features as it is. It can use for various kinds of applications which harnessed each features.

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TECHNICAL PROBLEM

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[Description of the Prior Art] Conventionally, the acrylamide (meta) system polymer is mainly manufactured by aqueous polymerization, and is obtained in the state of a uniform water solution. Moreover, in aqueous polymerization, since a product serves as gel which carried out water and handling becomes it is remarkable and difficult as monomer concentration becomes high, what has high monomer concentration cannot be manufactured industrially.

[0003] Therefore, although an acrylamide (meta) system polymer is diluted, and it is provided as a low concentration solution or disintegration is dried and carried out, in dealing with it by low concentration, an transportation cost becomes high, and heat energy huge for desiccation disintegration is needed uneconomically, and also it has problems, like insolubilization by thermal three-dimensions bridge formation takes place.

[0004] Moreover, although the manufacture approach of the dispersion liquid of the acrylamide system polymer by the emulsion polymerization of a water-in-oil type or the suspension polymerization in the inside of a hydrophobic solvent is also learned, since the hydrophobic organic solvent currently used by these approaches has a strong odor while it is dangerous, it has problems, like a large amount of costs are needed for each manufacturing facility of a polymerization and separation from the problem of work environment. It is known from before that water soluble polymers, such as an acrylamide (meta) system polymer, will cause other water soluble polymers and interactions underwater, and will produce phase separation on the other hand. For example, for example, if a polyalkylene glycol solution and a polyacrylamide water solution are mixed, phase separation will arise. However, only by applying the interaction reported, the dispersion liquid of the acrylamide system polymer which is rich in dispersibility and a fluidity (meta) are not obtained, and since we were anxious about the effect of the water soluble polymer together put on product performance, they have not resulted in utilization.

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## MEANS

[Means for Solving the Problem] this invention persons repeated examination wholeheartedly about the manufacture approach of an acrylamide (meta) system polymer from such a background. consequently, when a crosslinked polymer electrolyte is made to absorb the water solution containing the polymerization nature monomer which uses acrylamide (meta) as a principal component and it carries out a polymerization In order that the acrylamide (meta) system polymer generated with advance of a polymerization may carry out phase separation by the interaction with a crosslinked polymer electrolyte into a crosslinked polymer electrolyte, may deposit in the shape of a particle one by one and may form uneven structure, Even when a polymerization nature monomer was high concentration, the thing from which the water solution containing the polymerization nature monomer absorbed in the crosslinked polymer electrolyte hyperviscosity-izes to gel, and prevents advance of a polymerization and for which an acrylamide system polymer can be manufactured that there is nothing (meta) was found out. This invention is completed based on the starting new knowledge.

[0006] That is, this invention relates acrylamide to a crosslinked polymer electrolyte as a polymerization nature monomer (meta) at independent or (meta) the manufacture approach of an acrylamide system polymer characterized by carrying out the polymerization of the polymerization nature monomer into the crosslinked polymer electrolyte which was made to absorb the water solution which comes to contain acrylamide, acrylamide (meta), a kind to copolymerize, or two sorts or more of polymerization nature monomers, and was swollen (meta).

[0007] In this invention, acrylamide is used as an indispensable component as a polymerization nature monomer (meta). (Meta) acrylamide -- the thing of acrylamide and/or methacrylamide -- saying -- this invention -- setting (meta) -- it is the same semantics as the following. Generally, acrylamide is used. \*\* (meta) acrylamide can be used independently, and also it can also be used together with acrylamide (meta), a kind to copolymerize, or two sorts or more of polymerization nature monomers. (Meta) As acrylamide and a polymerization nature monomer to copolymerize, at least one sort chosen from an anionic partial saturation monomer, a cationic partial saturation monomer, a nonionic partial saturation monomer, and a cross-linking partial saturation monomer is raised.

[0008] As an anionic partial saturation monomer, alkali-metal salts, such as sodium salt of organic sulfonic-acids [, such as dicarboxylic acid; vinyl sulfonic acids such as monocarboxylic acid; maleic acids, such as an acrylic acid, a crotonic acid, and an allyl compound (meta) carboxylic acid, boletic acid, an itaconic acid, and muconic acid, a styrene sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, and an allyl compound (meta) sulfonic acid, ]; or these various organic acids and potassium salt, etc. are raised, for example (meta), it is independent in these one sort, or two or more sorts can be used.

[0009] As a cationic partial saturation monomer, to a typical thing, dimethylaminoethyl (meta) acrylate, Diethylaminoethyl (meta) acrylate, dimethylaminopropyl (meta) acrylamide, The partial saturation monomers which have the third class amino groups, such as diethylamino propyl (meta) acrylamide and allylamine (meta), or those hydrochloric acids, The salts of inorganic acids, such as a sulfuric acid and an acetic acid, or an organic acid, or this the third class amino-group content partial saturation monomer and methyl chloride, The partial saturation monomer

containing the quarternary ammonium salt obtained by the reaction with the fourth class-ized agents, such as benzyl chloride, a dimethyl sulfate, and epichlorohydrin, etc. is raised, it is independent in these kinds, or two or more sorts can be used.

[0010] As a nonionic partial saturation monomer, the alkyl ester (carbon numbers 1-8 of an alkyl group) of said anionic partial saturation monomer, acrylonitrile, styrene, vinyl acetate, the methyl vinyl ether, allyl alcohol (meta), etc. are raised. These are independent in a kind or can use two or more sorts.

[0011] Moreover, the following are raised as a typical thing of a cross-linking partial saturation monomer. As a 2 functionality partial saturation monomer, for example, ethylene GURIKORUJI (meta) acrylate, Di(meth)acrylate, such as diethylene GURIKORUJI (meta) acrylate and TORIECHIRENGURIKORUJI (meta) acrylate Methylenebis (meta) acrylamide, ethylene screw (meta) acrylamide, Screw (meta) acrylamides, such as hexa methylenebis (meta) acrylamide Divinyl ester, such as an adipic-acid divinyl and a sebacic-acid divinyl Allyl compound (meta) (meta) acrylate and epoxy (meta) acrylate Urethane (meta) acrylate, N-methylol (meta) acrylamide, JI (meta) allylamine, JI (meta) allyl compound dimethylannmonium, JI (meta) allyl compound phthalate, a JI (meta) allyl compound KUROREN date, a divinylbenzene, etc. are raised. As a 3 functionality monomer, moreover, 1, 3, 5-Tori (meta) acryloyl hexahydro-S-triazine, Tori (meta) allyl compound isocyanurate, the Tori (meta) allylamine, Tori (meta) allyl compound trimellitate, N, and N-JI (meta) allyl compound (meta) acrylamide etc. as a 4 functionality partial saturation monomer Tetramethylolmethane tetrapod (meta) acrylate, tetrapod (meta) allyl compound pyromellitate, N and N, N', N'-tetrapod (meta) allyl compound-1,4-diaminobutane, a tetrapod (meta) allylamine salt, tetrapod (meta) allyloxy ethane, etc. are raised. These are independent in a kind or can use two or more sorts.

[0012] the total mol sum of the polymerization nature monomer in which the amount of the aforementioned (meta) acrylamide and the polymerization nature monomer used to copolymerize contains acrylamide (meta) -- usually -- less than [ 50 mol % ] -- it is less than [ 20 mol % ] preferably. (Meta) Since the rate of acrylamide decreases when the amount of acrylamide and the polymerization nature monomer used to copolymerize exceeds 50-mol % (meta), the phase separation by the interaction with a crosslinked polymer electrolyte stops arising, and the particle of an acrylamide (meta) system polymer is no longer obtained. in addition, the application of the acrylamide system polymer with which an anionic partial saturation monomer, a cationic partial saturation monomer, a nonionic partial saturation monomer, and a cross-linking partial saturation monomer can be used together with acrylamide (meta) combining a kind or two sorts or more, respectively, and the operating rate is obtained (meta) etc. -- taking into consideration -- the total mol sum of a polymerization nature monomer -- usually -- 50-mol% of within the limits -- proper -- determining -- \*\*\*\*ing . However, when using a cross-linking partial saturation monomer, it is good less than [ of the total mol sum of a polymerization nature monomer / usual 10 mol % ], and to consider as 0.01-5-mol % preferably. In exceeding ten-mol %, in order that the whole water solution containing the polymerization nature monomer absorbed in the crosslinked polymer electrolyte may construct a bridge, the particle of an acrylamide (meta) system polymer is not obtained.

[0013] In this invention, the salt of the various polymer bridge formation objects obtained by carrying out the polymerization of a kind of the anionic partial saturation monomer of said instantiation which has a carboxylic acid and/or a sulfonic acid, for example or two sorts or more, and the cross-linking partial saturation monomer as a crosslinked polymer electrolyte which makes the polymerization nature monomer which uses acrylamide (meta) as a principal component absorb is raised. As an anionic partial saturation monomer, an acrylic acid is desirable. Moreover, as a cross-linking partial saturation monomer, ethylene GURIKORUJI (meta) acrylate etc. is desirable also in said instantiation. The amount of the amount of cross-linking partial saturation single used is suitably determined in consideration of the water-absorption-power force of a crosslinked polymer electrolyte, and is usually about [ of the total mol sum of the partial saturation monomer which constitutes a crosslinked polymer electrolyte ] 0.05-5 mol %.

[0014] If the water-absorption-power force of this crosslinked polymer electrolyte is extent

which can take the condition of happening only in the crosslinked polymer electrolyte with which the polymerization of the polymerization nature monomer which could absorb to homogeneity at the whole crosslinked polymer electrolyte, and was absorbed swelled the water solution containing a polymerization nature monomer, especially a limit will not be carried out but will usually be preferably made into five to 20 times about 1 to 100 times. In order that a crosslinked polymer electrolyte cannot absorb the water solution with which the water-absorption-power force contains a polymerization nature monomer in less than 1 time and the polymerization of a polymerization nature monomer may break out by underwater [ besides a crosslinked polymer electrolyte ], a hyperviscous gel object is obtained and it is not desirable. Moreover, when the water-absorption-power force exceeds 100 times and the water solution which contains a polymerization nature monomer in a crosslinked polymer electrolyte is added, while the location where the water solution concerned will be absorbed by only the contact front face with a crosslinked polymer electrolyte, and a polymerization advances in a crosslinked polymer electrolyte becomes an ununiformity, since the presentation ratio of the crosslinked polymer electrolyte and polymerization nature monomer which were set up, and water is changed, it is not desirable. In addition, the water-absorption-power force is the value which put the crosslinked polymer electrolyte into the ion exchange water of an overlarge, filtered after 30 minutes, and was calculated by the degree type. Water-absorption-power force (twice) = (weight of ion exchange water with which crosslinked polymer electrolyte absorbed water) / (weight of a polyelectrolyte).

[0015] Moreover, what copolymerized at least one sort which will use together with an anionic partial saturation monomer if it is within the limits in which the acrylamide system polymer obtained (meta) deposits by the shape of a particle by the interaction with the crosslinked polymer electrolyte concerned, and is chosen from amide group content partial saturation monomers, such as a cationic partial saturation monomer of said instantiation, a nonionic partial saturation monomer, and acrylamide (meta), is sufficient as the crosslinked polymer electrolyte of this invention. usually, the total mol sum of the partial saturation monomer from which the rate of the copolymerization monomer used together with an anionic partial saturation monomer constitutes a crosslinked polymer electrolyte -- receiving -- usually -- less than [ 30 mol % ] -- it is less than [ 10 mol % ] preferably. Moreover, what reformed the front face of a crosslinked polymer electrolyte by the cross linking agent which has a carboxylic acid etc. and two or more functional groups which react is sufficient as the crosslinked polymer electrolyte of this invention.

[0016] Although especially the class of salt of the polymer bridge formation object which constitutes a crosslinked polymer electrolyte is not limited, in this invention, alkali-metal salts, such as sodium salt or potassium salt, are desirable. moreover, the neutralization index of a carboxylic acid and/or a sulfonic acid -- usually -- 60-100-mol % -- it is 70-100-mol % preferably. It takes place [ formation of the particle of the acrylamide system polymer according / a neutralization index / to an interaction (meta) ] easily and is not usually desirable less than [ 60 mol % ]. In addition, formation of carboxylate and/or a sulfonate may be performed in the phase of an anionic partial saturation monomer, and you may carry out, after manufacturing a polymer bridge formation object. That is, as a crosslinked polymer electrolyte of this invention, it is desirable to use the alkali-metal salt of an acrylic-acid system polymer bridge formation object.

[0017] Next, the manufacture approach of the acrylamide (meta) system polymer of this invention is explained in detail. although the amount of the crosslinked polymer electrolyte used changes with a presentation and degree of cross linking of the crosslinked polymer electrolyte concerned, the presentation ratio of a polymerization nature monomer, polymerization concentration, and other polymerization conditions -- usually -- the weight ratio of a crosslinked polymer electrolyte and a polymerization nature monomer -- usually -- the former / latter = 10 / 90 - 90/10 -- it is 20 / 80 - 80/20 preferably. If the rate of a crosslinked polymer electrolyte separates from this range, an acrylamide (meta) system polymer cannot be obtained by the shape of a particle in a crosslinked polymer electrolyte.

[0018] Moreover, the water-solution concentration of a polymerization nature monomer is

usually 15 – 40 % of the weight preferably five to 50% of the weight. It is not desirable in order for a rate of polymerization to become quick too much, and for it to become impossible to control polymerization temperature by generation of heat, and for it to become impossible for a crosslinked polymer electrolyte to fully absorb the water solution of a polymerization nature monomer and to concur with the polymerization in the crosslinked polymer electrolyte exterior, if water-solution concentration exceeds 50 % of the weight. A rate of polymerization becomes extremely slow, and the phase separation by the interaction of the acrylamide (meta) system polymer and crosslinked polymer electrolyte which were generated stops arising, and it becomes impossible moreover, for it to become impossible to obtain the amount (meta) acrylamide system polymer of macromolecules, and to obtain an acrylamide (meta) system polymer according to the shape of a particle at less than 5 % of the weight.

[0019] The method of carrying out the polymerization of said polymerization nature monomer, and manufacturing an acrylamide (meta) system polymer makes the water solution containing a polymerization nature monomer absorb to a crosslinked polymer electrolyte, and can adopt various well-known approaches and the same approach as it conventionally except for performing a polymerization in the swollen crosslinked polymer electrolyte. For example, a crosslinked polymer electrolyte, a polymerization nature monomer, and water are taught to a predetermined reaction container, the usual radical polymerization initiators, such as a redox system polymerization initiator of the form which combined persulfate, such as potassium persulfate and ammonium persulfate, or these and the reducing agent like a sodium hydrogensulfite, are added, and the approach of warming, the approach of adding and carrying out UV irradiation of the photopolymerization initiator, etc. are raised under churning.

[0020] The amount used, such as a radical polymerization initiator, is usually 0.01–10–mol % to a polymerization nature monomer. moreover, pH of the crosslinked polymer electrolyte water solution containing the polymerization nature monomer at the time of a polymerization -- usually -- 6–10 -- it is 7–8 preferably, and it is necessary to set up the neutralization index of the carboxylic acid of said crosslinked polymer electrolyte, and/or a sulfonic acid so that it may go into this range Since it produces hydrolysis of an acrylamide system polymer in phase separation's stopping being able to happen easily when pH is lower than 6, and exceeding 10 (meta), it is not desirable. Although the temperature of a polymerization changes with presentations and those concentration of the class of radical polymerization initiator, a polymerization nature monomer, and a crosslinked polymer electrolyte and it cannot generally \*\*\*\*\*, it is usually within the limits of 25–90 degrees C, and a polymerization is performed to the bottom of such a condition for 1 to 12 hours. In addition, on the occasion of a polymerization, a water-soluble chain transfer agent, a surfactant, a salt, etc. can be used for arbitration as an additive if needed. Although the amount of these additives used changes with applications of the acrylamide system polymer obtained (meta) etc. and cannot be limited especially, generally it is 10 or less % of the weight to a polymerization nature monomer.

[0021] The weight average molecular weight of the acrylamide (meta) system polymer obtained in this way is usually 100,000 to about 20 million. Moreover, an acrylamide (meta) system polymer produces phase separation by the interaction with a crosslinked polymer electrolyte, and deposits by the shape of a particle in the swollen crosslinked polymer electrolyte. The particle of the obtained acrylamide (meta) system polymer is in the condition contained in the crosslinked polymer electrolyte, and direct drying can be carried out by warm air etc., or it can be made to be able to dry, after permuting by water soluble solvents, such as an acetone and a methanol, and it can also be fine-particles-ized. Moreover, the acrylamide (meta) system polymer contained by the shape of a particle in the crosslinked polymer electrolyte is gradually eluted by switching on a crosslinked polymer electrolyte underwater. (Meta) The temperature of water, pH, salt concentration, etc. can adjust the rate at which an acrylamide system polymer is eluted.



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EXAMPLE

[Example] Although an example explains this invention concretely below, this invention is not limited to this.

[0023] 200g (11.62 times as many water-absorption-power force as this) of example 1 sodium-polyacrylate bridge formation object powder was put into 3L reaction containers which attached a stirrer, nitrogen installation tubing, the thermometer, and the reflux condenser, after making the water solution which becomes this from acrylamide 100g, 700g of ion exchange water, and 0.8g of ammonium persulfates add and swell, except for dissolved oxygen, 3.5g of sodium-pyrosulfite water solutions was added 1% of the weight through nitrogen gas at the room temperature, and the polymerization was carried out at 45 degrees C under churning for 6 hours. The product was supplied in the acetone of 2L after polymerization termination, and the polyacrylamide particle in filtration and the condition of having carried out reduced pressure drying and having contained in the crosslinked polymer electrolyte was obtained. The weight of the dry matter (product) concerned was 289g, and the water-absorption-power force was 7.62 times. The electron microscope photograph of the dry matter concerned is as being shown in drawing 1 , and it is admitted that the polyacrylamide particle exists in the condition of having contained in the crosslinked polymer electrolyte.

[0024] 200g (9.54 times as many water-absorption-power force as this) of example 2 sodium-polyacrylate bridge formation object powder It puts into 3L reaction containers which attached a stirrer, nitrogen installation tubing, the thermometer, and the reflux condenser. To this, acrylamide 100g, methylenebis acrylamide 1.08g, After making the water solution which consists of 8.68g of sodium methallylsulfonate, 700g of ion exchange water, and 0.8g of ammonium persulfates add and swell, Except for dissolved oxygen, 3.5g of sodium-pyrosulfite water solutions was added 1% of the weight through nitrogen gas at the room temperature, and the polymerization was carried out at 45 degrees C under churning for 6 hours. The product was supplied in the acetone of 2L after polymerization termination, and the polyacrylamide particle in filtration and the condition of having carried out reduced pressure drying and having contained in the crosslinked polymer electrolyte was obtained. The weight of the dry matter (product) concerned was 301g, and the water-absorption-power force was 4.9 times. The electron microscope photograph of the dry matter concerned is as being shown in drawing 2 , and it is admitted that the polyacrylamide particle exists in the condition of having contained in the crosslinked polymer electrolyte.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is a 20100 times as many electron microscope photograph as the product obtained in the example 1.

[Drawing 2] It is a 50000 times as many electron microscope photograph as the product obtained in the example 2.

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[Translation done.]

\* NOTICES \*

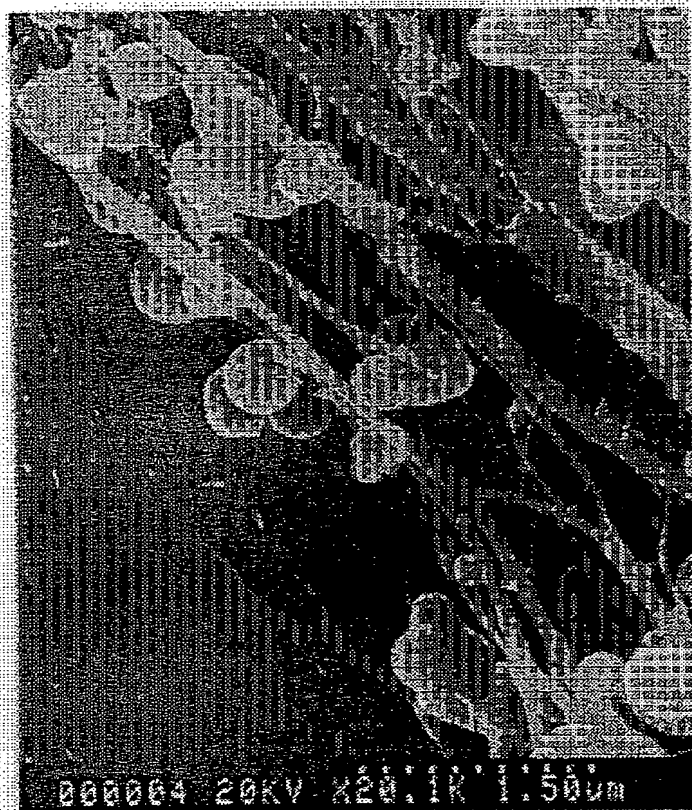
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DRAWINGS

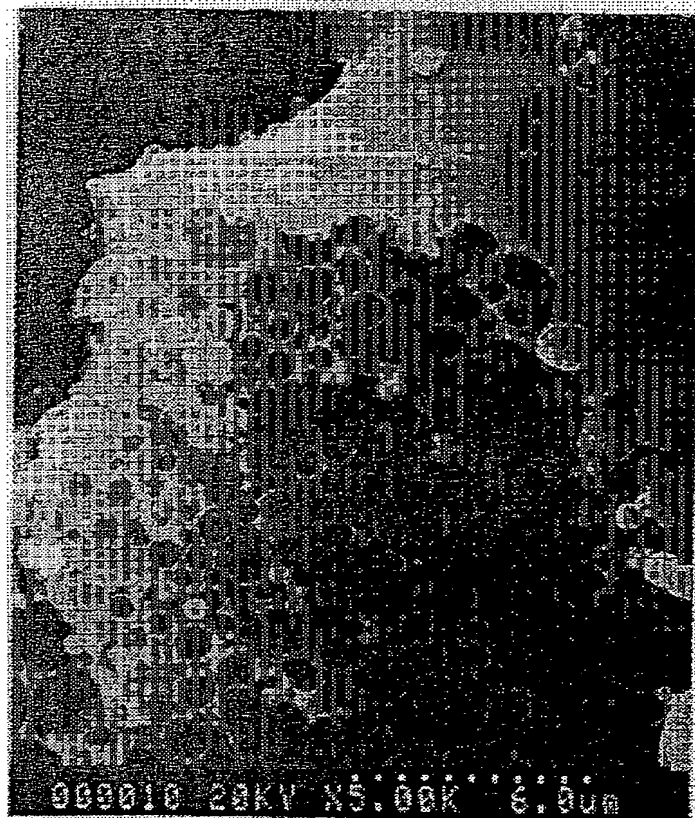
[Drawing 1]

図画代用写真



[Drawing 2]

図画代用写真



[Translation done.]